

The University of Chicago

AN X-RAY INVESTIGATION
OF THE STRUCTURE OF LIQUID
ORGANIC ALCOHOLS
AND ACIDS

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1938

By

DONALD PATTEN MacMILLAN

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D. P. MacM.

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INTRODUCTION

The study of x-ray diffraction has been a fruitful means of obtaining information about matter in its various states, and the study of x-ray scattering by liquids is pursued currently as a means of obtaining new information about the liquid phase. In a word, the point of theoretical interest at which this research was aimed was the explanation of a certain diffraction peak known in the language of the field as the "inner peak," and obtained not from all liquids, but only from a limited variety of types. With the answer to that problem in hand, it became possible to suggest structures for the space array of molecules in a number of kinds of liquids. Experimental data were required for the study, and feeling that existing data were in some respects incomplete and in others untrustworthy for our purposes, it became necessary to develop the apparatus and technique for taking x-ray liquid diffraction photographs.

CHAPTER I

HISTORICAL

The studies of liquid and of crystal diffraction originated at the same time, and though the latter science developed swiftly into a powerful tool for investigation, interest in liquid diffraction, after a brief flurry, subsided until a few years ago. While testing the predictions of von Laue's theory of diffraction by crystalline substances, Friedrich and Knipping¹ seem to have included a few amorphous materials. Friedrich was surprised to discover that these latter gave rise to diffraction rings, and he reported some further experiments including paraffin wax, paraffin oil, Canada balsam, and amber. In his discussion he pointed out the analogy to passage of light through a turbid medium, or to the halos of sun and moon. As an alternative explanation he suggested that tiny crystals might be responsible for the observed diffraction. Debye and also Ehrenfest asserted that interference must occur even in amorphous substances, due not only to the recurrence of a definite distance of approach, but also to interference of scattered radiation from different atoms of the same molecule.

Debye and Scherrer² thought that the scattering of finely ground crystals should be similar to that of a liquid. They, of course, overlooked the profound effect of limiting scattering centers to a certain few directions as in the case of a crystal, no matter how tiny it may be, as contrasted with the situation of a single molecule which may have neighbors in any direction whatever. The great dissimilarity of results for liquid and powder discouraged, but by no means entirely put aside the crystal theory for liquid diffraction, for there was the objection that a crystal could not be ground sufficiently fine to simulate the condition of a liquid.

¹W. Friedrich, Physik. Z., 14, 317 (1913).

²P. Debye and P. Scherrer, Nachr. d. Königl. Gesell. d. Wiss. zu Göttingen (1916), 1.

Along these same lines were experiments by de Broglie and Friedel,³ who attempted to find evidence of crystallinity in liquid crystals. The alkali metal oleates were found to give a good pattern consisting of several rings. Although the method of calculation is not mentioned it is safe to assume that the Bragg law was employed to calculate a so-called planar spacing of 43.6Å corresponding to the innermost diffraction ring. This is very probably the ring now known as the inner peak, and as far as it is possible to tell from the published data it is the first instance of its observation. Faint rings of larger diameter were ascribed to interference within the molecules. It seems unfortunate that the authors failed to show either photographs or tabulated data.

Experiments carried out in many laboratories during the period 1921-28, on a large number of liquids, showed diffraction to be given by all liquids. For a time there was argument as to whether the observed diffraction could be accounted for solely by scattering within the molecules, but the findings of Keesom and de Smèdt,⁴ who showed that liquid oxygen, nitrogen, and argon all yielded diffraction patterns, indicated that it is quite impossible for all the observed diffraction to be intramolecular.

Following the general development already outlined, the work of G. W. Stewart more or less dominated the field of liquid diffraction for a time, and under his leadership a better understanding of the liquid state emerged. Using the ionization chamber technique and filtered Mo K_α radiation, Stewart⁵ made a quantitative investigation of the diffraction of successive members of various homologous series of organic compounds. In a paper dealing with the diffraction of primary normal alcohols of from one to eleven carbon atoms, the curves for intensity vs. diffraction angle show a large main peak, and, at smaller angle, a lesser peak which has come to be known as the "inner peak." An error, persistent in the literature of liquid diffraction, was committed in the use of the Bragg law to calculate the spacing

³M. de Broglie and E. Friedel, Compt. rend., 176, 738 (1923).

⁴W. H. Keesom and J. DeSmèdt, Proc. Roy. Acad. Amst., 25, 118 (1922).

⁵G. W. Stewart and R. M. Morrow, Phys. Rev., 30, 232 (1927).

responsible for the observed scattering, under the misapprehension that some single distance was responsible for each diffraction peak. A graph of the main peak position against the number of carbon atoms reveals the fact that the main peak changes its position but little, and seems to approach a limiting position as the chain becomes longer. The suggestion was offered, and seems to have withstood the test of time and further investigation, that immediately neighboring molecules tend to line up parallel to one another, and that the main peak is due to the recurrence of the distance, roughly $4.6\text{\AA}$, from one molecule to its neighbors. The position of the inner peak was found to vary by a definite increment for each additional carbon atom added to the chain, the increment being, on the basis of the Bragg law, $1.54\text{\AA}$. Stewart deduced that the molecules must be associated end to end, so that the distance responsible for the inner peak was the COOH to COOH distance of double molecules. To account for the observed density he assumed that the COOH groups lie in 111 planes with respect to the axis of the molecule. To describe this condition Stewart introduced the term "cybotactic state." In it there is at once mobility of the molecules, and at the same time a certain degree of space array in which particular orientations of neighboring molecules are more probable than others, and some distances of separation recur more frequently than others.

Stewart's arguments against the belief that liquid diffraction is due to tiny crystals were several. In the first place if a crystal were disrupted enough to become a liquid, it means that forces of thermal agitation must exceed the binding forces within the crystal, and, that being the case, there is no reason to suppose that small fragments would be better able to exist than the whole crystal. In the second place the observed grating spaces of the solid and liquid are not equal. Finally, one may consider the resolving power of a crystal as calculated by the formula

$$h = 2 \left(\frac{L \lambda^2}{\pi} \right)^{\frac{1}{2}} \left(\frac{\lambda}{L} \right) \left(\cos \frac{\theta}{2} \right)^{-1};$$

where h is the width of the diffraction peak at half maximum, and L the length of edge of the crystal. For lauryl alcohol, for example, the value of h is 8.8° , giving for L the value 14×10^{-8} cm. The absurdity of a crystal of that size is obvious.

In another of his contributions Stewart, together with

Skinner,⁶ reported examination of several isomers of alcohols previously mentioned. In further substantiation of the view that the inner peak is due to the length of the double molecule, it was discovered that where the hydroxyl group is not attached on the terminal or next the terminal carbon atom of the chain, the inner peak was moved to the larger angle corresponding to the length of a single molecule. The evident explanation, of course, would be that end to end association is impeded unless the hydroxyl group is nearly terminal. A possible explanation of weaker outlying rings is suggested for the first time in this paper. Two proposals are made, first that they are higher orders of the main peak, and second that they may be due to scattering from within the molecule itself. The two outer rings of the observed diffraction pattern correspond to Bragg spacings of 1.11 and 2.50Å, which might well be the distance of first and second removed neighbors within the molecule. Diffraction measurements on liquid normal fatty acids⁷ showed that here too the position of the inner peak indicates the double molecule. Likewise, as might be expected, it was discovered that in the case of diffraction by liquid normal paraffins⁸ there is no inner peak. Noteworthy too is the fact that the position of the main peak remains unaltered for acids, alcohols, and paraffins, thus further bolstering the already well-established interpretation of the main peak as a manifestation of the diameter of the molecule.

Zernicke and Prins⁹ must be credited with development of the method of treatment now applied to liquid diffraction problems. They state clearly that the observed diffraction is due to a superposition of interference from three sources; (a) electrons within the atom, (b) atoms within the molecule, and (c) molecules in relation to one another. Assuming that all orientations of the molecule are equally probable, and introducing a radial distribution function to take account of the greater prevalence of certain interatomic distances, they developed a relation between the radial distribution of atoms and the observed scattering of x-rays.

⁶G. W. Stewart and E. W. Skinner, Phys. Rev., 31, 1 (1928).

⁷R. M. Morrow, Phys. Rev., 31, 10 (1928).

⁸G. W. Stewart, Phys. Rev., 31, 174 (1928).

⁹F. Zernicke and J. A. Prins, Z. Physik, 41, 184 (1927).

The method was successfully applied by Debye and Menke¹⁰ to a study of the x-ray scattering of liquid mercury.

Warren¹¹ analyzed Stewart's diffraction curves for normal paraffins according to the method set up by Zernicke and Prins. At the start of his paper Warren showed conclusively that the Ehrenfest-Keesom equation previously used in the treatment of liquid diffraction is inapplicable to any but spherical molecules. In forming the following picture of the liquid state his assumptions were that the molecules are roughly cylindrical, and arranged in approximate hexagonal close packing with a distance of about $5\text{\AA}$ separating the axes of neighboring molecules. The distance, $5\text{\AA}$, is derived by calculation from molecular weight, density, and the length of the carbon chain as determined by measurements of the crystalline paraffins, and is in agreement with the value obtained by Adam in surface film experiments. It will be observed (Fig. 1), that the distance from any given atom to its neighbors in the next chain is not a perfectly definite figure, but rather that a number of distances near $5\text{\AA}$ occur frequently.

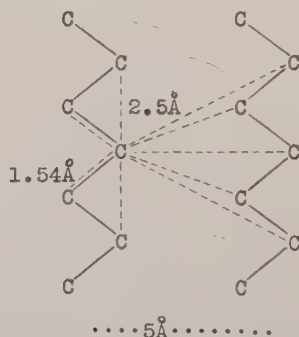


Fig. 1.--Parallel Alignment of Molecules According to Warren

Thus at distances in the vicinity of $5\text{\AA}$ there is a marked excess of scattering matter above the average. Likewise within the molecule itself two neighbors are to be found at $1.54\text{\AA}$, two at $2.50\text{\AA}$ and so on, and it is to be expected that these excesses of scat-

¹⁰P. Debye and H. Menke, Erg. der Tech. Roentgenkunde, 2, 1 (1931).

¹¹B. E. Warren, Phys. Rev., 44, 969 (1933).

tering matter will give rise to diffraction peaks.¹² On the basis of the foregoing concept of liquid structure Warren calculated the approximate scattering curve to be expected of a paraffin and found it to agree satisfactorily with the curve obtained experimentally by Stewart. The essential difference between Warren's and Stewart's interpretations lies in Stewart's use of the Bragg law and his tacit assumption of a temporary arrangement of molecules in planes, as in a crystal. Thus Stewart relates the main peak to a single distance, Warren to a distance that is more probable than the average.

¹²W. C. Pierce, J. Chem. Phys., 3, 252 (1935), has shown that these distances may be obtained from a Fourier analysis of a complete scattering curve for a n-paraffin.

CHAPTER II

THEORY

The derivation to be given follows the notation used by Zachariasen,¹³ and arrives at a relation between the scattered intensity of radiation expressed as a function of scattering angle, and the radial distribution of atoms responsible for it. The starting point is a consideration of the x-rays scattered by any atom whose position with respect to a fixed origin in the liquid is described by the vector $\underline{r}_n$ (Fig. 2). The unit vector $\underline{s}_0$ represents the direction of the incident x-ray beam, which we shall consider to be lineally polarized perpendicular to the plane of the paper and of electric intensity E_0 . The unit vector

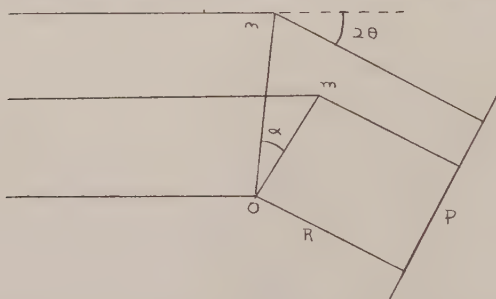


Fig. 2.--X-ray Scattering by a Group of Atoms

$\underline{s}$ has the direction of the scattered ray under observation at the point P, which is also in the plane of the paper and at a distance R from the origin. The scattered ray from the nth atom may be represented by the expression

$$A = \frac{e^2 E_0}{R m c^2} f_n e^{i \frac{2\pi}{\lambda} (\underline{s} - \underline{s}_0) \cdot \underline{r}_n} \quad \text{Eq. 1}$$

The factor $\frac{e^2 E_0}{R m c^2}$ is the scattering power of a single electron, and, when multiplied by the atomic structure factor, f_n , gives the scattered amplitude from the atom. The exponential function is a phase factor, $(\underline{s} - \underline{s}_0) \cdot \underline{r}_n$ being the path difference between

¹³W. H. Zachariasen, J. Chem. Phys., **3**, 158 (1935).

the ray scattered by the n th atom and a reference ray going from the origin to P. The total amplitude scattered to P is obtained by summing over all n atoms.

$$A_P = \frac{e^2 E_0}{R m c^2} \sum_n f_n e^{i \frac{2\pi}{\lambda} (\underline{s} - \underline{s}_0) \cdot \underline{r}_n} \quad \text{Eq. 2}$$

The intensity of a ray is, by definition, the number of ergs per square centimeter flowing past a given point in a second. Since it is well known that the energy of an electromagnetic field per cubic centimeter is $\frac{A^2}{4\pi}$, multiplication by c must give the instantaneous intensity. The average intensity will then be $\frac{c A^2}{8\pi}$. Since unpolarized radiation is used it is also necessary to multiply by the factor

$$\frac{1 + \cos^2 \theta}{2},$$

where 2θ is the scattering angle. To find the scattered intensity from an atom, form A_P^* , the conjugate complex quantity to A_P .

$$A_P^* = \frac{e^2 E_0}{R m c^2} \sum_n f_n e^{-i \frac{2\pi}{\lambda} (\underline{s} - \underline{s}_0) \cdot \underline{r}_n} \quad \text{Eq. 3}$$

Then

$$I_P = \frac{c}{8\pi} \frac{e^4 E_0^2}{R^2 m^2 c^4} \frac{1 + \cos^2 2\theta}{2} \sum_n \sum_m f_n f_m e^{i \frac{2\pi}{\lambda} (\underline{s} - \underline{s}_0) \cdot (\underline{r}_n - \underline{r}_m)} \quad \text{Eq. 4}$$

This expression may be somewhat simplified by lumping together the constants

$$\frac{c}{8\pi} \frac{e^4 E_0^2}{R^2 m^2 c^4} \frac{1 + \cos^2 2\theta}{2}$$

as the Thompson factor, symbolized by T . To simplify the exponential we may make use of the fact that $\underline{s} - \underline{s}_0 = 2 \sin \theta$, and representing the angle between $(\underline{s} - \underline{s}_0)$ and $(\underline{r}_n - \underline{r}_m)$ by α we have

$$I_P = T \sum_n \sum_m f_n f_m e^{i \frac{4\pi}{\lambda} \sin \theta |\underline{r}_n - \underline{r}_m| \cos \alpha} \quad \text{Eq. 5}$$

If we let $k = \frac{4\pi}{\lambda} \sin \theta$, and write $|\underline{r}_n - \underline{r}_m|$ as r_{nm} , the instantaneous intensity becomes

$$I_P = T \sum_n \sum_m f_n f_m e^{i k r_{nm} \cos \alpha} \quad \text{Eq. 6}$$

We assume that the atoms may take on all possible positions, therefore to find the average intensity $\bar{I}$, all orientations of $(\underline{r}_n - \underline{r}_m)$ must be considered equally probable. The probability of finding an angle between α and $\alpha + d\alpha$ is

$$\frac{1}{2} \sin \alpha d\alpha$$

Therefore

$$\bar{I} = T \sum_n \sum_m f_n f_m \int_0^\pi \frac{1}{2} \sin \alpha d\alpha e^{i k r_{nm} \cos \alpha} \quad \text{Eq. 7}$$

$$\bar{I} = T \sum_m \sum_n f_n f_m \frac{\sin Kr_{nm}}{Kr_{nm}} \quad \text{Eq. 8}$$

If we assume that the atoms are all alike so that $f_n = f_m$, and further that on the average they all have the same surroundings, it is possible to introduce further simplification by reduction of the above expression to a single sum taken N times.

$$\bar{I} = TNf^2 \left[1 + \sum_N \frac{\sin Kr_m}{Kr_m} \right] \quad \text{Eq. 9}$$

The summation may now be replaced by a continuously variable radial distribution function $p(r)$ which expresses the probability of finding an atom between r and $(r + dr)$ from any given point. Thus

$$\bar{I} = TNf^2 \left[1 + \int_0^\infty p(r) \frac{\sin Kr}{Kr} dr \right]. \quad \text{Eq. 10}$$

In order to avoid the practical necessity of integrating to infinity, we may split up $p(r)$ into two parts, which may be looked upon as an average term plus an excess or deficit term so that

$$p(r) = 4\pi r^2 \rho + q(r);$$

where ρ is the number of atoms per cubic centimeter. In practice it will be found that the integral of $q(r)$ converges rapidly to a limiting value at reasonably small values of r .

$$\bar{I} = TNf^2 \left[\int_0^\infty 4\pi r^2 \rho \frac{\sin Kr}{Kr} dr + 1 + \int_0^\infty q(r) \frac{\sin Kr}{Kr} dr \right] \quad \text{Eq. 11}$$

The first integral is zero unless $k = 0$, which corresponds to scattering at zero angle, in which case the value of the integral is N . Since we are interested in observing scattering only at angles other than zero, we shall ignore the first term. Then

$$\bar{I} = TNf^2 \left[1 + \int_0^\infty q(r) \frac{\sin Kr}{Kr} dr \right] \quad \text{Eq. 12}$$

In Eq. 12 we have an implicit solution to the problem, because $q(r)$ is the desired answer, while $\bar{I}$ is the observed quantity. Fortunately the desired inversion may be accomplished by the Fourier Integral Theorem which states that

$$\text{if } f(y) = \int_0^\infty f(x) \sin xy \, dx, \quad \text{Eq. 13}$$

$$\text{then } f(x) = \frac{2}{\pi} \int_0^\infty f(y) \sin xy \, dy. \quad \text{Eq. 14}$$

Rearranging Eq. 12 and then applying the theorem we have

$$\begin{aligned} \frac{\bar{I}}{NTf^2} - 1 &= \int_0^\infty q(r) \frac{\sin Kr}{Kr} dr, \\ q(r) &= \frac{2r}{\pi} \int_0^\infty K \left[\frac{\bar{I}}{NTf^2} - 1 \right] \sin Kr dk \end{aligned} \quad \text{Eq. 15}$$

The treatment of observed scattering data begins with correction for polarization, following which the scattered intensity is graphed as a function of s , a variable chosen for convenience in the calculations to come

$$s = \frac{2 \sin \theta}{\lambda}$$

It must not be forgotten that $\bar{I}$ as spoken of in the preceding derivation refers only to the coherent part of the scattered radiation, so that in the treatment of experimentally observed intensities we must subtract the intensity due to incoherent scattering. This incoherent radiation is given by an expression due to Wentzel¹⁴

$$I_{inc} = NT \left[Z - \sum f_n^2 \right] \quad \text{Eq. 16}$$

At large angles of scattering the intensity fluctuation is rapidly damped and becomes insignificant due to the trigonometric term $\frac{\sin Kr}{Kr}$, which is tantamount to saying that at large angles the scattering by a liquid becomes equal to that of a gas. Making use of the expression $\bar{I} \approx NTf^2$, and of the fact that $I_{obs} = \bar{I} + I_{inc}$, the coherent and incoherent scattering are calculated for some large angle and their sum equated to the observed scattering at a point midway between a maximum and a minimum. A graph of the incoherent scattering can now be drawn in to proper scale and subtracted from the total observed radiation. Dividing the resultant coherent scattering by f^2 yields a quantity designated for convenience by E , from which the function $k(E-1)$ is formulated.

$$E = \frac{I_{obs} - I_{inc}}{f^2} \quad \text{Eq. 17}$$

A graph of $k(E-1)$ against k is made to such scale that $k = 2\pi$ occurs at forty centimeters from the origin on the x axis

¹⁴Compton and Allison, "X-rays In Theory and Experiment," D. Van Nostrand Co., Inc., New York, 1935, p. 135.

in order to facilitate the use of the harmonic analyzer¹⁵ to obtain the integrals of Equation 19. This is done in the following manner. A single valued function $y = f(x)$ is expressible as the sum of sine and cosine terms.

$$y = a_0 + a_1 \sin x + a_2 \sin 2x + \dots + a_n \sin nx \quad \text{Eq. 18} \\ + b_1 \cos x + b_2 \cos 2x + \dots + b_n \cos nx$$

The coefficients, a_n , are related to y and x by the equation

$$a_n = \frac{1}{\pi} \int_0^{2\pi} f(x) \sin nx \, dx. \quad \text{Eq. 19}$$

Since the desired integral,

$$q(r) = \frac{2r}{\pi} \int_0^{2\pi} K[E-1] \sin Kr \, dk, \quad \text{Eq. 20}$$

is of the same form, it follows that the harmonic analyzer may be used to perform the integration mechanically. Inasmuch as what we wish to know is the number of atoms to be found at a given value of r , we have only to set $n = r$ and evaluate the integral for the desired values of n to obtain the required points for construction of the $q(r)$ graph. To evaluate for fractional values of r , eg. $r = 0.5$ etc., the curve $k(E-1)$ is replotted to one half the original scale so that the point $k = 4\pi$ now comes at forty centimeters from the origin on the x axis. Then successive coefficients, a_n , will correspond to values of $q(r)$ at $r = 0.5, 1.0, 1.5$ etc.

¹⁵Available through the kindness of Professor Henry Schultz of the Economics Department, University of Chicago.

¹⁶Equation 15 may be written

$$q(r) = \frac{2r}{\pi} \int_0^{2\pi} K[E-1] \sin Kr \, dk + \frac{2r}{\pi} \int_{2\pi}^{\infty} K[E-1] \sin Kr \, dk.$$

Although the $(E-1)$ curve does not cease oscillating at values of k greater than 2π , in practice it has been found that negligible error is introduced by assuming the integral from 2π to infinity to be zero. In preparing the graph of $k(E-1)$ vs. k it is necessary to bring the curve to $k(E-1) = 0$ at 40 cm. from the origin on the x -axis in order to comply with the requirements imposed by the harmonic analyzer.

CHAPTER III

EXPERIMENTAL

For several reasons it was felt that new data on the scattering of alcohols and acids were advisable. The previous work by Stewart suffered from the fact that the curves had not been carried out to sufficiently large angles. In addition it might be objected that only filtered, and not strictly monochromatic radiation, had been employed. Likewise, whenever the ionization chamber method of measuring intensities is used there is always the possibility of error due to variations in x-ray intensity. Accordingly, in the construction of our apparatus, an effort was made to avoid all these objections.

The x-ray source consisted of a metal tube of compact design with a rock salt monochromator built in, the design of which has previously been described.¹⁷ It was partly by virtue of the short x-ray path from target to sample that it was possible to obtain an intense beam of Cu K α radiation.

The camera itself (Fig. 3) had to be fairly gas tight because of the necessity of replacing the air within it by hydrogen in order to avoid excessive gas scattering. A continuous flow of hydrogen was required to sweep out the vapor of the sample. Inasmuch as the pressure difference between inside and outside was negligible, it was possible to use cellophane windows to permit entry of x-rays and likewise to cover a slot one centimeter high which was cut out of the camera for most of its circumference to permit observation out to scattering angles of 142°. The film could then be wrapped around the outside of the camera, and need not be subjected to the atmosphere of hydrogen within, nor need the camera be opened to place or remove film. The film was protected from visible light by a layer of black paper, and fluorescent rays from the sample were partially filtered out by a layer of aluminum foil wrapped with the film.

¹⁷W. C. Pierce, C. M. Olson, and D. P. MacMillan, Rev. Sci. Inst., **8**, 145 (1937).

The main beam of x-rays had to be trapped to prevent fogging the film (see Fig. 3). Adjustment of the trap was a rather delicate matter, for the geometry of the situation was such that a shallow trap must be used to avoid shading the film at small angles. On the other hand such a shallow trap failed to prevent

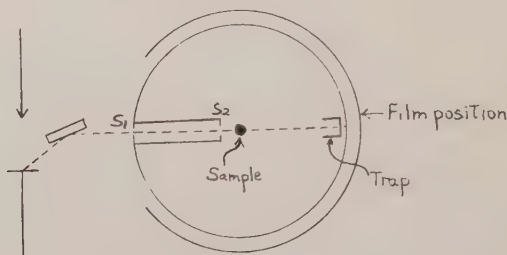


Fig. 3.--X-ray Tube and Camera

stray radiation from reaching the film at larger angles. Because of this, coupled with the difficulty of recording the widely different intensities of scattering at large and at small angles on one piece of film, it was deemed advisable to take separate pictures for large and for small angles, thereby permitting the use of an effective trap for each of the two conditions. The defining slits in the camera required some care, for of course scattering from the edge of the first or beam defining slit, S_1 , must not be permitted to reach the film. Therefore the beam passes into an enclosed chamber, and thence through S_2 , which it must not touch, for if it did so further stray scattering would occur.

In previous researches the samples to be studied have sometimes been held in containers, and alternatively have been used in the form of a thin stream of liquid flowing from a jet, and consequently free of containing walls. The advantage of the former method is that it permits the use of a very small quantity of liquid, but it suffers from the defect that unless a rather thick sample is used, scattering by the container is of considerable magnitude. From the point of view of absorption correction it would be desirable to use a thin cell with parallel windows front and back. For our purposes the employment of a cell of this type presented two drawbacks. It was difficult to find a non-crystalline wall material that could be obtained sufficiently thin and yet of material such that both it and the adhesive used to

stick it to its supporting structure would withstand water, alcohols, and organic acids. Thin glass capillaries offered possibilities, but were discarded not only because of the difficulty of getting them thin enough, but because slight variation in the position of the capillary with respect to the x-ray beam would cause great changes in the scattering of the container unless the cross section of the capillary were much greater than that of the beam, or else the beam completely bathed the capillary. Neither of these conditions was desirable for our purposes.

Particularly in view of the fact that the substances proposed for study gave promise of being available in sufficient quantity, a pumping system was constructed to effect continuous circulation of the liquid. Flowing out of the jet in a smooth cylinder about 0.8 mm. in diameter, the liquid falls into a trap and thence flows back to the pumping mechanism. The pump is essentially like that described by Katzoff,¹⁸ and is one in which the liquid being pumped touches none but glass surfaces.

The substances were purified by fractional distillation using an eight ball Schnyder column, after which the purity of the sample was checked by measurement of its refractive index. Purity data are listed below.

	Published B.P.	Boiling Range	Refractive Index Published	Refractive Index of Sample
n-Propyl alcohol....	97.8	96.4-97.0	1.3954	1.3856
Propionic acid.....	141	139.6-140.4	1.3874	1.3864
n-Hexyl alcohol.....	155.8	155.8-156.7	1.4161	1.4177
Caproic acid ¹⁹	202	199.2-201.7	1.4163	1.4161
Ethyl propionate....	Eimer and Amend--Absolute; not purified further.			
n-Octanol ²⁰	Not purified further.			

A sample of the substance to be studied passed in a smooth stream, 0.8 mm. in diameter, through the center of the camera, whose diameter was 10.82 cm. The scattered intensity from a sam-

¹⁸S. Katzoff, *J. Chem. Phys.*, **2**, 841 (1934).

¹⁹By kindness of Mr. H. B. Near, Northwest Chemical Co., Wawatosa, Wisconsin.

²⁰By kindness of Dr. E. Emmett Reed, Johns Hopkins University.

ple was photographed on two separate films, one to include scattering angles up to thirty-five degrees and taken with a shallow trap, the second, taken with a deep trap, overlapping the first and extending on out to a hundred and forty degrees. Exposure of from four to seven hours resulted in a blackening²¹ of seven on the main peak, while seven hours sufficed to produce a blackening of three in pictures of large angle scattering. To obtain these results, the x-ray tube was operated on rectified alternating current at about twenty-five milliamperes and thirty kilovolts. The x-ray beam was rendered approximately monochromatic by reflection from a crystal of rock salt, and had a width of about 0.5 mm. when passing through the sample.

²¹The significance of the term "blackening" is defined by Eq. 21.

CHAPTER IV

CALCULATIONS

As is customary, the film material was Eastman Duplitized X-ray film, and it was processed in Eastman X-ray Developer. Following previous experience, the troublesome matter of correcting for the relation of blackening to intensity of x-rays was avoided by remaining within the linear portion of the film characteristic curve, which has been proved to permit operation up to seven times the blackening (see Eq. 21) of unexposed film. Blackenings were measured by a modified Dershem type of photoelectric microphotometer.²² It is used as a drift rate instrument wherein the accumulation of charge on an electrometer vane caused a spot of light reflected from the vane mirror to move across a scale. The time required for the spot to traverse an arbitrary distance was measured by means of a stopwatch made by Venner Time Switches Ltd., London. The stopwatch itself is deserving of some comment, for it has thirty escapements per second and consequently permitted measurement to 0.03 seconds. When the operator had developed the requisite skill it was possible to obtain checks showing an average deviation of the order of 0.03 seconds on times ranging from ten to twenty-five seconds. Consequently the accuracy was about 0.25%, which was considered satisfactory.

It is assumed that each quantum of x-rays striking the film affects the same number of silver halide grains in the emulsion, and that consequently the blackening of the film is proportional to x-ray intensity. Furthermore, the absorption of light passing through the film during photometering is assumed to obey Beer's law, so that provided the photometer is operated over the linear portion of its characteristic, the drift rate of the electrometer is dependent upon the intensity of x-rays. Symbolically;

Number of developed silver grains $\approx$ Blackening $\approx I_x$, Eq. 21
where I_x represents the intensity of x-rays.

²²E. Dershem, Rev. Sci. Inst., 3, 43 (1932).

Likewise $T_{\text{obs}} \approx e^{(\text{Blackening})}$,

and therefore $T_{\text{obs}} \approx e^{I_x}$. Eq. 22

Suppose that for a portion of practically unexposed film we find the drift rate time T_0 , then

$$T_0 \approx e^{I_0} = 1 \quad (\text{since } I_0 = 0).$$

The ratio of x-ray intensities will be given by

$$\frac{I_x}{I_0} = \log \frac{T_x}{T_0} \quad \text{or} \quad I_x = \log T_x. \quad \text{Eq. 23}$$

Computation of results was facilitated by conversion of all observed times to their logarithms, following which the logarithm of the drift time obtained on the blank film was subtracted. Notwithstanding the fact that the light source used on the microphotometer was operated from a storage battery at less than the rated voltage, there was always a slow change in illumination due to blackening of the lamp bulb and to temperature effects. By observing the drift time for the light transmitted by a reference point at frequent intervals, it was possible to correct accurately for the instrument drift.

The observed intensity for each angle was corrected by subtraction of the intensity due to stray scattering, as determined from a blank film. The blank was determined by making an exposure without liquid but with all other conditions identical with those employed in liquid exposures. One factor, the scattering due to vapor of the liquid, was not present in the blank, but in all liquid exposures a rapid stream of hydrogen was maintained through the camera in order to sweep out the vapor.

Every film provided two independent sets of scattering values, for the two halves of the film should be symmetrical about zero angle. The photometer readings, corrected to x-ray intensity, were plotted as a function of angle, and an average taken of the two sides of the curve. The agreement between the two sides of the film was close in all cases. Only one film was made for the large angle scattering of each substance; however, the two sides of the film usually differed by less than 12%. For smaller angle photographs several check determinations were made, ranging in number from two for octyl alcohol and ethyl propionate, to five for propyl alcohol. The average deviations of the

intensity curves were rarely more than 6% and often the curves became practically indistinguishable even on large scale graphs.

The observed scattering, after subtraction of the blank, was corrected for polarization by dividing by the factor for Cu K α rays reflected from a crystal

$$P = \frac{1 + .723 \cos^2 2\theta}{2}$$

Eq. 24

It was necessary to find out whether or not corrections were necessary for absorption of x-rays by the sample, and since the sample was not completely bathed by the beam it was impossible to use existing tables. The calculation for hexyl alcohol was carried out in the following fashion. The cross section of the jet was represented by a circle 10 cm. in diameter divided up into elements of area 5 mm. square by drawing vertical and horizontal lines through it. A is a number proportional to the amount of scattering matter in an element of volume, and is taken to be unity if the element is a complete square, or the appropriate fraction if it is not. The contribution of the i th element of the R th column is then

$$dI_1 = X_R A_i e^{-ux_i}, \quad \text{Eq. 25}$$

where X_R is the incident x-ray intensity on the R th column, u is the linear absorption coefficient of the liquid, and x is the length of the x-ray path within the jet.

The linear absorption coefficient for hexyl alcohol had to be calculated from the mass absorption coefficients for carbon, hydrogen, and oxygen at the wavelength of Cu K α radiation. Representing the mass absorption coefficients of carbon, oxygen, and hydrogen by u_c , u_o , and u_h , the mass absorption, u_m , for hexyl alcohol is given by

$$u_m = \frac{6 u_c (\text{at.wt. carbon}) + 1 u_o (\text{at.wt. oxygen}) + 14 u_h (\text{at.wt. hydrogen})}{(\text{molecular weight of hexyl alcohol})} \quad \text{Eq. 26}$$

The desired linear absorption coefficient of hexyl alcohol, u , is then given by

$$u = \frac{u_m}{\rho} = 4.10, \quad \text{Eq. 27}$$

where ρ is the density of hexyl alcohol.

The model was used as follows. Measurement of the distance from the periphery of the circle to the given element, plus the distance from there to the point of emergence of the scattered

ray at the desired angle gives a number which is proportional to length of x-ray path for that volume element. Successive steps lead readily to a table of e^{-ux_1} for each volume element scattering to the given angle. The entire calculation is repeated for angles of 0, 30, 60, 90, 120, 150, 180 degrees. Then the total intensity scattered by the Rth column at each angle consists of a summation of the scattering of the 1 elements of which it is composed;

$$I_R = \sum_l X_R A_l e^{-ux_1} \quad \text{Eq. 28}$$

Since the x-ray beam was not perfectly uniform, the distribution of intensity in its cross section was determined by photographing and photometering. The scattering power of each of the R columns composing the jet was then multiplied by the appropriate value of X_R , as determined from the intensity graph of the beam. Following this weighting process it is possible to find the total intensity scattered to each of the given angles as

$$I = \sum_R I_R \quad \text{Eq. 29}$$

The maximum difference between the scattered intensities at different angles is found to be 1.3%, which means that the absorption correction can be ignored.

It was also desired to test the hypothesis that if the beam is displaced somewhat so that it strikes the jet unsymmetrically, the differing intensity scattered to the two sides of the film will be taken care of by averaging. The intensity was calculated with the beam, whose width at half maximum was about 0.5 mm., displaced first to the right 0.2 mm., and then to the left 0.2 mm. The two intensities were averaged and compared with that obtained by proper placement of the sample. As can be seen from the following tabulation, the misplacement of sample causes no significant difference in absorption, so it was considered justifiable to entirely omit the absorption correction.

Scattering Angle	Jet Correctly Placed $\sum I_R$	Jet to Right $\sum I_R$	Jet to Left $\sum I_R$	Average of Left and Right
0	939	943	935	939
30	939	920	956	938
60	946	909	974	941
90	951	908	984	946
120	952	917	979	948
150	949	931	965	948
180	948	951	944	948

After analysis of the scattering by hexyl alcohol (Fig. 4) had been carried through by the method outlined, the resultant $q(r)$ curve shown in Figure 5 was compared with the $q(r)$ curve¹² similarly obtained from Katzoff's data on n-heptane¹⁸. It was expected that the $q(r)$ curve for hexyl alcohol would show a maximum at some large value of r attributable to the length of either the single or the associated molecule. Unexpectedly, it did not, but was found to be very similar to the $q(r)$ curves for heptane and for rubber.²³ Accordingly the intensity curve for heptane was subtracted from that of hexyl alcohol and the resulting difference, shown by the shaded portion of the graph, Figure 4, was subjected to Fourier analysis.

$$q(r)_{alc} = \frac{2r}{\pi} \int_0^{2\pi} K[E-1] \sin Kr \, dk$$

$$q(r)_{par} = \frac{2r}{\pi} \int_0^{2\pi} K[E-1] \sin Kr \, dk$$

The difference is

$$q'(r) = q(r)_{alc} - q(r)_{par} = \frac{2r}{\pi} \int_0^{2\pi} K[E_{alc} - E_{par}] \sin Kr \, dk \quad \text{Eq. 30}$$

The resulting $q'(r)$ (Fig. 5) was found to be identical with the difference between the $q(r)$ curve of hexyl alcohol and that of heptane. It will be seen that the $q'(r)$ curve shows an excess of scattering matter from $r = 0$ to $6.8\text{\AA}$, a deficit from $r = 6.8$ to $13.3\text{\AA}$, and is rapidly damped out at larger values of r .

²³G. L. Simard and B. E. Warren, J. Am. Chem. Soc., **58**, 507 (1936).

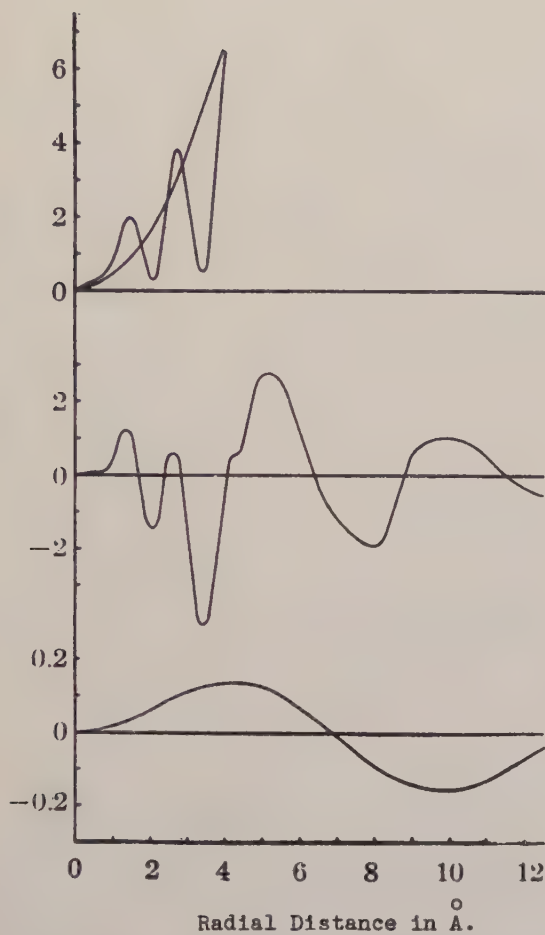


Fig. 5.--Atomic Distribution for n-Hexyl Alcohol: Upper Curve, Total Number of Atoms; Center Curve, $q(r)$; Lower Curve, $q'(r)$, Enlarged Scale.

CHAPTER V

DISCUSSION

The intensity curves shown in Figure 6 are corrected for everything save incoherent scattering. The following observations may be made by examination of them:

1. The position of the main peak remains fairly constant, which is in keeping with the explanation offered by Warren, in which he showed that the main peak is caused by parallel arrangement of neighboring molecules.

2. A comparison of scattering curves for octyl, hexyl, and propyl alcohol shows that the inner peak moves to smaller angle with increasing length of the carbon chain and becomes more sharply defined.

3. The inner peak for an alcohol occurs at smaller angle than for the corresponding acid.

4. The inner peak is sharper for alcohols than for acids.

5. Comparison of the curves for propionic and caproic acids shows that the peak at $s = 0.4$ to 0.5 is found at somewhat smaller angle for shorter chain compounds.

6. The peak at $s = 0.4$ is more pronounced in acids than in alcohols.

7. An ester fails to show the inner peak.

In arriving at an hypothetical structure for the space array occurring in the alcohols and acids such as have been studied here, it is necessary to maintain consistency with a number of lines of evidence. The strong tendency toward parallel alignment of neighboring molecules must be considered. Of course, any structure proposed must agree with the $q(r)$ curves. In particular the structure of esters and paraffins, which fail to show the inner peak, must differ from that for alcohols and acids, which do show that peak, in some manner in keeping with the $q(r)$ curves.

Hydrogen bridge formation between COH groups is known to be responsible for association of many types of compounds, and

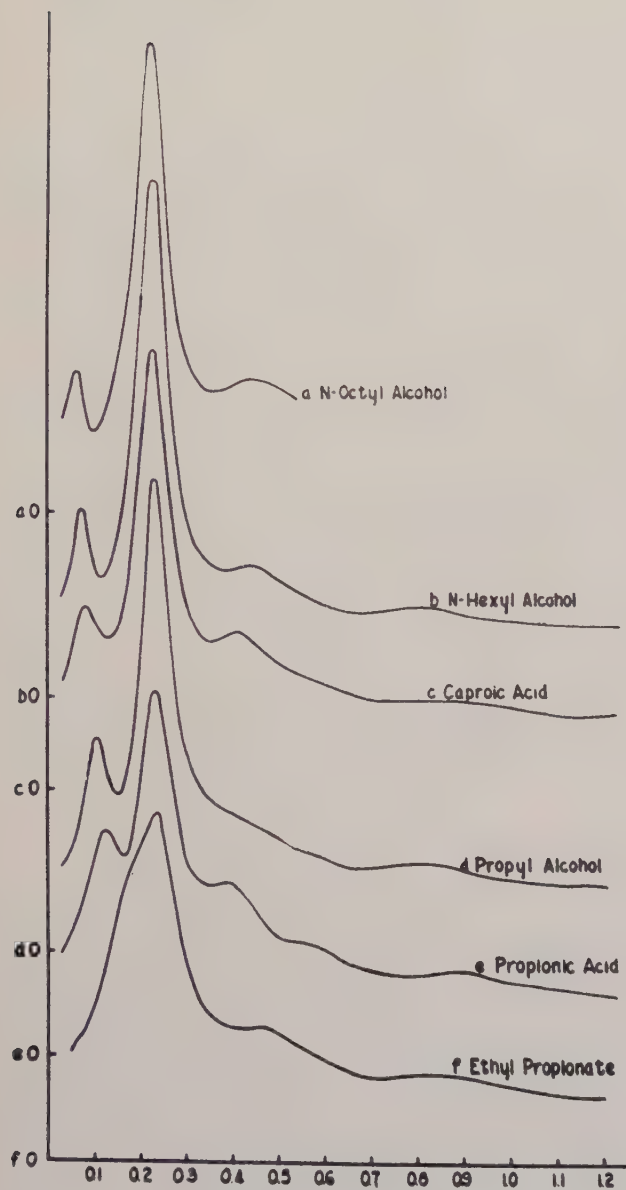


Fig. 6.--X-ray Scattering Curves

among these are organic alcohols and acids.^{24, 25} Eötvös constant determinations for pure liquids and cryoscopic measurements of dilute solutions in both polar and non-polar solvents make it appear that acids form dimers by association, while alcohols associate in some more complex manner.

The molecular volumes of alcohol and acid of the same number of carbon atoms are virtually identical for chains longer than two carbon atoms, and consistently less than that of the paraffin having an equal number of carbon atoms. Now it is known by the position of the main peak that the cross section of all these molecules is the same, therefore it follows that the end gap between one molecule of a paraffin and the next must be different from the gap between corresponding acid or alcohol molecules. The volume increase of these chain compounds is found to be about $26.2\text{\AA}^3$ for each CH_2 group added. Measurements on crystalline solids show the increment of length of the chain to be $1.25\text{\AA}$ per carbon atom, and with this assumption the length of a paraffin molecule of n carbon atoms may be written

$$L = 1.25 (n-1) + 3.85. \quad \text{Eq.31}$$

For the single acid or alcohol molecule

$$L = 1.25 (n-1) + 3.40. \quad \text{Eq.32}$$

In these expressions the constants $3.85\text{\AA}$, and $3.40\text{\AA}$ represent the end gap between the ends of the molecules as shown by Figure 7:



Fig. 7.--The End Gap Between Paraffin Molecules

But we know that the molecules of alcohol and acid are associated, therefore the end gap $3.40\text{\AA}$ is a mean value for the polar and non-polar ends. Assuming the end gap between non-polar ends of associated groups to be the same as it is in the case of paraffins, the length of the dimer associated molecule is given by

²⁴M. L. Huggins, J. Org. Chem., 1, 407 (1937).

²⁵E. N. Lassettre, Chem. Rev., 20, 259 (1937).

$$L = 2 \times 1.25 (n-1) + 3.85 + 2.95 \quad \text{Eq. 33}$$

The significance of the number $2.95\text{\AA}$ is shown by Figure 8.

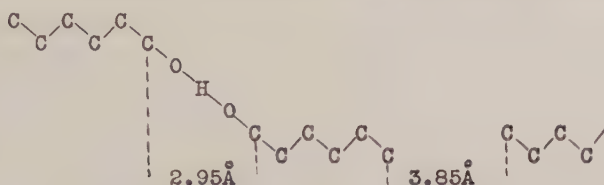


Fig. 8.--The End Gap in Alcohols or Acids

Any proposed structures for alcohols and acids must satisfy the requirements of the above discussion of molecular dimensions.

In the search for possible structures, mechanical models were practically indispensable. It was assumed that; (1) the C-C distance is $1.54\text{\AA}$ with tetrahedral angles between bonds; (2) the C-O distance is $1.4\text{\AA}$ with a tetrahedral angle for singly bound oxygen; (3) the O-H-O distance is 2.6 to $2.8\text{\AA}$ with oxygen valence angles of 120° and hydrogen valence angles of 180° . A fragment of the proposed structure for alcohols is shown in Figure 9 as it would appear projected on the plane of the paper.

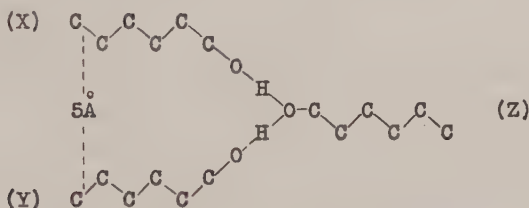


Fig. 9.--Space Array of an Alcohol

The molecules X and Y are considered to be in the plane of the paper, while Z is parallel to it but about 1.5 to $2.0\text{\AA}$ above. While this structure may be extended somewhat by further addition of alcohol molecules, it is probably not capable of infinite extent because of the slight distortion of bond angles that must occur in order to permit more molecules to lie parallel to those already present.

This structure is in harmony with the geometrical requirements above, and likewise satisfies the condition that the radial distribution of atoms agree with the $q(r)$ function for alcohols. There is a considerable concentration of oxygen atoms at the

center of the cluster, and it will be noted that these oxygen atoms have numerous neighbors at all distances up to the length of the single molecule, beyond which the end gap is responsible for a deficit. Conversely, the members of the carbon chain have oxygen atom neighbors not found in the paraffin. Thus, as shown by the $q(r)$ curve of the alcohol, there is a greater number of neighbors to be found at all distances up to half the diameter of the cluster, beyond which there is a deficit. Finally, it should be made clear that neither large clusters nor large planes rich in oxygen atoms are required to account for the observed scattering at small angles.

The dimer acid molecule may be represented as a projection on the plane of the paper as shown in Figure 10.

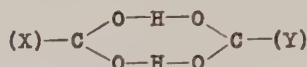


Fig. 10.--The Dimer Acid Molecule

The molecules X and Y lie in parallel planes with the O-H-O bridges running diagonally between the two planes. According to Pauling and Brockway,²⁶ the closed ring lies in a plane in the case of formic acid vapor, but in order to do this it is necessary to assume a C-C distance of 3.9Å. Particularly in view of the identical volume of alcohol and acid molecules the non-planar structure is favored.

Taken by itself, the acid dimer strongly resembles the ester molecule, for both have oxygen atoms near the center of the chain, yet the former shows an inner peak and the latter does not. It must then be that some further arrangement exists in the acid. In keeping with the requirements of the $q(r)$ curve, the structure shown in Figure 11 is suggested, in which the dimers are clustered so that the oxygen atoms are concentrated near the center.

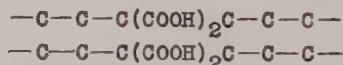


Fig. 11.--Cluster of Acid Dimers

The $q(r)$ curve of such an arrangement is highly similar to that of the alcohol and might be expected to give rise to an inner

²⁶L. Pauling and L. O. Brockway, Proc. Nat. Acad. Sci., 20, 336 (1934).

peak. Binding forces tending to hold such a cluster together must be slight since not only do Eötvös constant measurements for alcohol and acid show a more complex association for alcohols than for acids, but likewise at any given temperature the viscosity of an alcohol is greater than for the corresponding acid. In all discussions of orientation of molecules in liquids it need not be supposed that any regularity whatever may be expected to persist at a distance of several molecular diameters from any given point, and thermal agitation must give rise to considerable disarray even of closest neighbors.

Using the same type of explanation as for normal alcohols and acids, it is possible to explain the experimental results obtained by Stewart²⁷ for 1, 2, 3, and 4-octanol. He found that 4-octanol gave rise to a pronounced inner peak occurring at $s = 0.086$, whereas that for 1-octanol occurred at $s = 0.062$. The proposed structure for 4-octanol, when projected on the plane of the paper, appears in Figure 12. The cluster may be enlarged by further addition of alcohol molecules to give a structure highly resembling that of normal alcohols and acids. The concentration of oxygen atoms near the center accounts for an excess of scattering power up to approximately half the length of the single molecule, and thereby for the occurrence of the inner peak at larger angle than for the normal alcohol. The fact that only a slight inner peak is observed for 2, and for 3-octanol is on

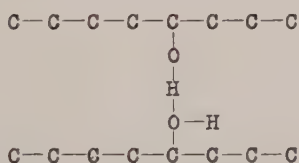


Fig. 12.--Association of 4-Octanol

account of the dissymmetry of the associated structure with consequent washing out of that part of the $q(r)$ curve responsible for the inner peak.

The third peak, occurring at approximately $s = 0.4$, is deserving of some comment. It may be attributed to a maximum in the $q(r)$ curve in the neighborhood of $2.7\text{\AA}$, and consequently must be regarded as a composite due to frequent recurrence of the O-O

²⁷G. W. Stewart, Phys. Rev., 35, 726 (1930).

distance of 2.6-2.8Å together with the distance of 2.5Å from each carbon atom to its second neighbor. It was observed that this third diffraction peak is more pronounced for acids than for alcohols, an effect particularly noticeable in shorter chain compounds. The observation is explicable if we remember that in the acid structure the O-O spacing occurs with greater frequency than in the alcohol, and hence would be expected to give rise to greater diffraction. It was also observed that this diffraction peak shifts to smaller angle with shorter chain acids. In long chain compounds the effect due to the longer O-O spacing of 2.6-2.8Å is largely overshadowed by the more common occurrence of the C-C spacing of 2.5Å, and the position of the third peak is consequently determined by the 2.5Å spacing. On the other hand when the chain is made shorter the O-O spacing becomes increasingly important so that the maximum of the $q(r)$ curve is pushed out to larger values of r , and the diffraction peak moves in to smaller angle.

